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(54) Title: IRRADIATION CONVERSION OF THERMOPLASTIC TO THERMOSET POLYMERS (57) Abstract Disclosed is a radiation-cross-linkable thermoplastic polymer composition, a process for the preparation thereof, an angioplasty balloon made using such a composition, and a method of using the angioplasty balloon. The composition contains a reactive monomer cross-linker facilitates cross-linking of the reaction product upon contact of the cross-linker-containing composition with a particle beam from a radiation source.		

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IRRADIATION CONVERSION OF THERMOPLASTIC TO THERMOSET POLYMERS

This invention relates generally to the conversion of thermoplastic polymers into thermoset polymers and more specifically to such thermoset
5 polymers exhibiting improved physical and chemical properties, relative to the corresponding thermoplastic polymers. Illustrative of such polymers are thermoset polyurethanes which are advantageously prepared using aliphatic diisocyanates and a reactive monomer crosslinker.

Thermoplastic polymers, such as thermoplastic polyurethanes, are
10 relatively easy to process into a wide variety of fabricated products. Unfortunately, however, the high temperature stability of these polymers and their physical properties such as mechanical strength at elevated temperatures, as well as their stability in some commonly-used organic solvents, are less than might be desired. Accordingly, methodology has been developed to provide heat-induced
15 crosslinking to convert thermoplastic polymers, such as thermoplastic polyurethanes, into thermoset polyurethanes having the desired stability at high temperatures and in the presence of solvents. By way of illustration, U.S. Patent 4,255,552 discloses thermoset polyurethane elastomers obtained by adding organic peroxides to a liquid polyurethane-forming composition prior to reacting
20 the composition to form the polyurethane. The '552 patent teaches that the liquid polyurethane-forming composition containing "unactivated hydrogen peroxide" may be formed into a desired article and then heated to thermoset the article, or provided in solid form such as sheet, crumbs, or granules which are then formed into a desired article that is then thermoset by heating the article. The organic
25 peroxides disclosed in the '552 patent are said to have a half-life of greater than one hour at 100°C. Unfortunately, these peroxide-containing compositions are less stable than might be desired during melt processing or thermoforming of the polyurethane composition into the desired finished article, thus providing technology that is not commercially practical.

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As an alternative to heat induced crosslinking of thermoplastic polyurethanes, their conversion into thermoset polyurethanes by irradiation is known in the art. A technical journal article entitled "Radiation Crosslinked Thermoplastic Polyurethane", published in the journal International Polymer Science and Technology, Vol. 19, No. 1, pp. T/6-T/9 (1992), discloses the production of such thermoset polyurethanes using a polyisocyanate and methacrylate monomer as a radiation-cross-linkable monomer. This technical journal article does not disclose the particular polyisocyanate used in making polyurethanes disclosed therein. Unfortunately, methacrylate is more heat sensitive than otherwise might be desired, causing a risk of premature cross-linking during storage, shipping, or processing, and prior to the desired conversion of the thermoplastic polyurethane into a thermoset polyurethane. Further, not all polyisocyanates perform alike in irradiation-crosslinking of TPUs. Indeed, the present inventor has been unsuccessful in attempts to cross-link TPU formulations based upon aromatic polyisocyanates to provide a desirable article. Instead of cross-linking, the resulting article exhibits an undesirable discoloration.

U.S. Patent No. 4,762,884 issued August 9, 1988 for "Process for the Production of Radiation-Crosslinked Thermoplastic Polyurethanes". This patent discloses the use of a cross-linking agent being a monomeric acrylate or methacrylates. These acrylates and methacrylates are more heat sensitive than might otherwise be desired. Further, although this patent discloses polyisocyanates generally, with a preference for aromatics, the present inventor (as pointed out hereinabove) has been unsuccessful in attempts to cross-link TPU formulations based upon aromatic polyisocyanates to provide a desirable article. As stated above, instead of cross-linking, the resulting article exhibits an undesirable discoloration.

Irradiation-induced cross-linking of other polymers, such as nylon, is known in the prior art, the use of these other polymers for property enhancement, such as the conversion of the nylon from a thermoplastic to a thermoset polymer in the form of an angioplasty balloon within the blood vessels of a human or other

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mammal, has not been disclosed heretofore to the knowledge of the present inventors.

In view of the above, there is a continuing need in the polymers manufacturing community for new polymer compositions that are readily thermoset by cross-linking when desired, but also less sensitive to unwanted heat-induced cross-linking during storage and prior to use than prior art compositions, such as the above-discussed prior art polyurethane-forming compositions, most notably prior art peroxide, acrylate, and methacrylate-containing compositions. Such compositions desirably would provide advantageous processing capability, such as by extrusion, when the composition is in the thermoplastic state, and advantageous elevated temperature stability and solvent resistance when the composition is thermoset after formation into the desired product. Moreover, new uses for compositions known to be cross-linkable in the presence of irradiation, such as nylon, would also be desirable. The present invention provides such desirable polymer compositions, together with processes for the production of the composition, as well as new uses for compositions known to be irradiation cross-linkable, such as nylon.

In one aspect, the present invention relates to a radiation-crosslinkable polymer composition characterized by:

(a) a polymer selected from the group consisting of polyurethanes, styrene-based polymers, polyester-based polymers, polyether-based polymers, polyamide-based polymers, polylaurinlactam-based polymers, polytetrahydrofuran-based polymers, and combinations thereof, and

(b) a reactive monomer for cross-linking at least a portion of said polymer upon contacting said reactive monomer energy, such as ionizing radiation particles, from a radiation source. The "polymer" referred to in component (a) is intended to encompass polymers characterized by the recited base component, as well as co-polymers containing the recited base component polymerized with a separate monomeric component. Preferably, the polymer of component (a)

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comprises a block co-polymer containing hard and soft segments. The "ionizing radiation particles" referred to in component (b) is intended to encompass any such particles, including photons, beta-particles and gamma-particles, or a combination thereof, emitted from a radiation source. Illustrative sources for such

5 "ionizing radiation particles" include electron-beam radiation, ultraviolet radiation, and combinations thereof.

In another aspect, the present invention relates to a radiation-crosslinkable thermoplastic polyurethane composition characterized by:

- (a) a polyurethane produced by reacting:
 - 10 (i) an aliphatic polyisocyanate, and
 - (ii) a polyah, and

- (b) a reactive monomer for cross-linking at least a portion of said polyurethane upon contacting said reactive monomer with ionizing radiation particles from a radiation source.

15 In still another aspect, the present invention relates to a process for preparing a thermoplastic article and for converting the thermoplastic article to a thermoset article, said process characterized by the steps of:

- (a) preparing a thermoplastic polymer product by mixing a solid, extrudable thermoplastic polymer product with a solid or liquid reactive monomer
- 20 cross-linker and a polymer selected from the group consisting of nylon, polyurethanes, styrene-based polymers, polyester-based polymers, polyether-based polymers, polyamide-based polymers, polyaurinlactam-based polymers, polytetrahydrofuran-based polymers, and combinations thereof, (advantageously, in one embodiment causing said solid thermoplastic polymer product to adsorb or
- 25 absorb liquid reactive monomer, thus providing a solid thermoplastic admixture),
- (b) forming said thermoplastic mixture into a desired thermoplastic article, and

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(c) irradiating said article with a particle beam in order to cause said reactive monomer cross-linker in said product to cross-link at least a portion of said polymer, thereby converting said article into a thermoset article, said thermoset article exhibiting enhanced properties, such as enhanced melt stability,
5 relative to said thermoplastic article.

In still another aspect, the present invention relates to a process for converting a thermoplastic polyurethane to a thermoset polyurethane. The process comprises the steps of:

(a) preparing a liquid or solid thermoplastic polyurethane composition
10 comprising a reactive monomer cross-linker and a reaction product of:

(i) an aliphatic polyisocyanate, and

(ii) a polyahl, and

(b) irradiating said composition with a particle beam (preferably a beam of photons) in order to cause said reactive monomer cross-linker in said composition
15 to cross-link at least a portion of said reaction product, thereby converting said composition into said thermoset polyurethane.

In yet another aspect, the present invention relates to a process for preparing a thermoplastic polyurethane and converting the thermoplastic polyurethane to a thermoset polyurethane comprising the steps of:

(a) preparing a liquid or solid thermoplastic polyurethane-forming
20 composition comprising a reactive monomer cross-linker and also comprising:

(i) an aliphatic polyisocyanate, and

(ii) a polyahl, and

(b) reacting said aliphatic polyisocyanate with said polyahl to form a
25 polyurethane composition containing said cross-linker, and

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(c) irradiating said polyurethane composition with a beam of photons in order to cause said reactive monomer cross-linker in said composition to cross-link at least a portion of said reaction product, thereby converting said composition into said thermoset polyurethane.

5 In yet another aspect, the present invention relates to a process for producing a thermoset product which comprises irradiating a thermoplastic elastomer composition containing a reactive monomer cross-linker in order to cross-link said thermoplastic elastomer to convert the thermoplastic elastomer to said thermoset product, said thermoplastic elastomer composition comprising a
10 component selected from the group consisting of styrenic co-polymers, co-polyester polymers, co-polyamide polymers, a reaction product of polyaurinlactam and polytetrahydrofuran, a reaction product of an aliphatic polyisocyanate and a polyahl; and, combinations thereof.

 In yet another aspect, the present invention relates to a cross-linkable
15 angioplasty balloon suitable for irradiation-induced cross-linking, said angioplasty balloon comprising a radiation-crosslinkable polymer composition comprising (a) a component selected from the group consisting of nylon, styrenic co-polymers, co-polyester polymers, co-polyamide polymers, a reaction product of polyaurinlactam and polytetrahydrofuran, a reaction product of an aliphatic
20 polyisocyanate and a polyahl; and, combinations thereof, and (b) a reactive monomer cross-linker in an amount sufficient to provide cross-linking of at least a portion of said polymer or copolymer upon contacting said cross-linker with ionizing photons from a radiation source.

 In yet another aspect, the present invention relates to a method of using an
25 angioplasty balloon that is produced from a thermoplastic polymer converted to a thermoset polymer, wherein the balloon comprises the reaction product of a radiation-crosslinkable polymer composition comprising (a) a component selected from the group consisting of nylon, poly(1,4-butanediol terephthalate), styrenic co-polymers, co-polyester polymers, co-polyamide polymers, a reaction product
30 of polyaurinlactam and polytetrahydrofuran, a reaction product of an aliphatic

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polyisocyanate and a polyahl; and, combinations thereof, and (b) a reactive monomer cross-linker in an amount sufficient to provide cross-linking of at least a portion of said polymer or copolymer upon contacting said cross-linker with radiation (such as free radical-initiating or ionizing photons) from a radiation source, said method comprising the steps of:

- (i) forming a tube from said radiation-crosslinkable polymer composition,
- (ii) irradiating said tube with a beam of particles in order to cause said radiation-crosslinkable polymer composition to crosslink, thereby converting said tube from a thermoplastic to a thermoset state, said thermoset state exhibiting enhanced properties relative to said thermoplastic state,
- (iii) heat expanding a portion of the tube to provide a balloon in said tube, and deflating said balloon,
- (iv) inserting said tube containing said balloon, in a deflated state, into a desired blood vessel within a human or other mammal body, and moving said balloon to a desired site within said blood vessel, and
- (v) inflating said balloon to an inflated state at said desired site to provide an inflated balloon.

In another aspect, the present invention relates to a process for fabricating a tube containing an angioplasty balloon from a crosslinkable polymer composition comprising (a) a component selected from the group consisting of nylon, poly(1,4-butanediol terephthalate), styrenic co-polymers, co-polyester polymers, co-polyamide polymers, a reaction product of polyaurinlactam and polytetrahydrofuran, a reaction product of an aliphatic polyisocyanate and a polyahl; and, combinations thereof, and (b) a reactive monomer cross-linker in an amount sufficient to provide cross-linking of at least a portion of said polymer or copolymer upon contacting said cross-linker with radiation (such as free radical-initiating or ionizing photons) from a radiation source, said process comprising the steps of:

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- (i) forming a tube from said radiation-crosslinkable polymer composition,
- (ii) irradiating said tube with a beam of particles in order to cause said radiation-crosslinkable polymer composition to crosslink, thereby converting said tube from a thermoplastic to a thermoset state, said thermoset state exhibiting enhanced properties relative to said thermoplastic state,
- (iii) heat expanding a portion of the tube to provide a balloon in said tube, and deflating said balloon, thus forming said tube containing said angioplasty balloon.

In another aspect, the present invention relates to the thermoset polymer products and the thermoset polyurethane products produced by the above-recited processes.

In still another aspect, the present invention relates to a method of forming a coated substrate comprising a substrate and an extrudable solid coating on said substrate, said method comprising applying said coating to said substrate in a thermoplastic state, and converting said coating to a thermoset state by free radical initiated crosslinking of the coating in the presence of radiation selected from the group consisting of electron beam radiation, uv radiation, or a combination thereof, to provide a thermoset coating on said substrate characterized by enhanced bonding efficacy to said substrate in said thermoset state relative to said thermoplastic state. The extrudable solid coating is suitably fabricated using a sheet coating, powder coating, or a molded or spray solid coating. Typical substrates include metal, glass, plastic, wood, paper, and combinations thereof. Typical coatings comprise a polymer selected from the group consisting of polyurethanes, styrene-based polymers, polyester-based polymers, polyether-based polymers, polyamide-based polymers, polylaurinlactam-based polymers, polytetrahydrofuran-based polymers, and combinations thereof.

In yet another aspect, the present invention relates to a method of forming a composite comprising two substrates with a coating therebetween, the

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improvement comprising contacting one side of each of said two substrates with said coating in a thermoplastic state, and converting said coating to a thermoplastic state by free radical initiated crosslinking of the coating in the presence of heat or particle beam radiation selected from the group consisting of
5 electron beam radiation, uv radiation, or a combination thereof, to provide said composite, wherein the thermoset coating in said composite is characterized by enhanced bonding efficacy to said two substrates relative to said thermoplastic state.

a method of forming a composite comprising a substrate and a coating on said
10 substrate, said method comprising applying said coating to said substrate in a thermoplastic state, and converting said coating to a thermoplastic state by free radical initiated crosslinking of the coating in the presence of heat or particle beam radiation selected from the group consisting of electron beam radiation, uv radiation, or a combination thereof.

15 Also disclosed are the coated substrates and composites produced by the above methods.

These and other aspects will become apparent upon reading the following detailed description of the invention.

It has now been surprisingly found, in accordance with the present
20 invention, that a wide variety of polymers and copolymers are suitably irradiated in the presence of specific monomeric radiation sensitizers in order to cause the polymer to crosslink, thereby enhancing the resistance of the polymer against thermal and chemical degradation caused by exposure to heat or corrosive chemicals. Advantageously, co-polymers are employed in the compositions of the
25 present invention, and the preferred co-polymers are so-called "block co-polymers". The block co-polymers contain discrete "hard" and "soft" segments that provide alternating aggregated and amorphous segments, respectively, by virtue of the specific combination of polymers employed in the co-polymer. Without wishing to be bound by any particular theory, it is believed that

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advantageous result associated with the use of block co-polymers, in accordance with the present invention, is attributable to the propensity for crosslinking induced by ionization radiation to occur primarily within the amorphous (i.e., the soft segment) matrix. Hence, the presence of the amorphous matrix in alternating regions throughout the polymer will promote the desired crosslinking throughout the polymer.

By way of background, block co-polymer-type thermoplastic elastomers exhibit the advantages of rubber-like elasticity and reversible melt transitions, thereby combining features of thermoplastics and rubbers without requiring vulcanization. These block co-polymer-type thermoplastic elastomers combine the further advantages of high melt temperature, low glass transition temperature, elasticity and thermoplasticity in one polymer. Blocks are formed by segregating each co-polymer into a specific polymer region. With proper sequencing and selection of co-polymer molecular weight, the polymer can exhibit the advantageous properties that characterize each block rather than an amalgamation of the unitized polymer. Block co-polymers are typically non random, and instead their backbone exhibits alternating sequences of hard and soft segments. "Hard" blocks reversibly self aggregate below the polymer melt temperature. Polymer tensile strength accrues from these aggregated regions within the polymer. The aggregation provided by virtue of these aggregated regions is reversible, hence these materials behave like they are thermoplastic polymers. Above the melt temperature, the polymer is a viscous liquid. This allows thermoplastic elastomers to be processed using conventional plastics processing equipment with the added advantage of recyclability of scrap that is produced during fabrication of the desired products. "Soft" blocks tend to accumulate in amorphous matrixes providing for regions of polymer elasticity at temperatures above the glass transition point.

There are distinct advantages associated with the ability to convert thermoplastic polymers, particularly block co-polymers, to thermoset polymers in accordance with the present invention. This ability to convert is particularly

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important since thermoplastic elastomers, in general, and block copolymers specifically, lack the wide temperature performance range of thermoset rubbers, and their compression set, solvent resistance and deformation resistance at high temperatures are generally not as good as the values for those properties as
5 obtained for thermoset elastomers. Thus, these deficiencies are mitigated, or avoided entirely, by virtue of the ready ability to convert thermoplastic elastomers into thermoset elastomers in accordance with the present invention.

As mentioned above, conversion of the thermoplastic to thermoset polymer is suitably effected using ionizing radiation particles, such as photons,
10 beta-particles and gamma-particles, or a combination thereof, emitted from a radiation source. Illustrative sources for such "ionizing radiation particles" include electron-beam radiation, ultraviolet ("uv") radiation, and combinations thereof. UV curing to provide the thermoset polymer is suitably effected using a photon (free radical) initiator, such as the allylic compounds and/or acrylates described
15 herein.

Illustrative copolymers useful in the present invention include (1) styrenic co-polymers including (a)SBS (styrenic polybutadienic), (b) SIS (styrenic polyisoprenic) and (c) S-EB-S (styrenic polyethylene-butylenic) copolymers; (2)
20 co-polyester polymers including copolymers of poly (1,4 butanediol terephthalate) and poly(alkylene ether terephthalate) trademarked under the HYTRIL mark, and (3) co-polyamide polymers including (a) copoly(ether-ester-amide) polymers trademarked under the PEBAX mark, and (b) PA12 elastomers being copolymers of polyaurinlactam and polytetrahydrofuran trademarked under the VESTAMID mark, and the like.

25 It has also been surprisingly found, in accordance with the present invention, that these polymers or copolymers, together with a radiation-sensitizing monomer, are suitable for fabricating angioplasty balloons made using thermoset tubing in accordance with the present invention. These balloons exhibit excellent properties, including resistance against breakage when the balloon is expanded in
30 a blood vessel to remove occlusions in the blood vessel. If, for example, the

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angioplasty balloon comprises S-EB-S (Styrenic polyethylene-butylenic) copolymer, the styrene hard segments of the co-polymer provide structural integrity to the balloon, and the amorphous poly(ethylene-butylene) segments provide flexibility to the balloon, an important characteristic during insertion of
5 the balloon into the desired blood vessel while in a thermoplastic state. This balloon also comprises a reactive monomer, e.g. triallylisocyanurate ("TAIC"), for crosslinking copolymer, such as the S-EB-S copolymer. Irradiation of the precursor tubing for making the balloon activates the reactive monomer and causes the amorphous poly(ethylene-butylene) segments to be preferentially
10 crosslinked to provide enhanced structural integrity to the balloon. The enhanced structural integrity of the balloon makes it resistant to breakage during use of the balloon to remove blockage in the blood vessels.

As additional illustrations, the present invention is suitably employed to prepare thermoplastic surgical gloves that, once irradiated to thermoset the glove
15 material, provides the gloves with enhanced structural integrity and resistance to breakage during use. Also envisioned are thermoset articles possessing a "memory" such as shrink- fitting surgical gloves that are stretched to an oversize before use, and caused to shrink fit tightly to the hand through the action of body heat or by contacting the gloves with warm water just before use. Likewise, the
20 present invention lends itself to use in male and female birth-control sheathes that can similarly be shrink fit plus will resist breakage during usage, or that can be thinner than those conventionally used while having similar (or greater) structural integrity.

In accordance with the present invention, a preferred thermoplastic
25 polymer, namely thermoplastic polyurethane (so-called "TPU") or polyurea or other polymer or co-polymer is suitably converted to a thermoset polyurethane or polyurea using a polymer-forming or preformed polymer in combination with a select reactive monomer that facilitates crosslinking with the polymer in the presence of irradiation. Illustratively, a polyurethane-forming or a preformed
30 polyurethane (or a polyurea-forming or preformed polyurea) composition

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comprising an aliphatic diisocyanate and a polyahl, or the reaction product thereof, together with a select reactive monomer (preferably an allylic monomer, more preferably an allylic monomer that is essentially free of peroxide, acrylate and methacrylate moieties) as a crosslinking promoter, are mixed and irradiated to provide the desired thermoset product after forming the product from the extrudable solid thermoplastic polymer raw material. Alternatively, the reactive monomer is suitably contacted with a polymer (or a polymer-forming composition for providing such polymer) selected from the group consisting of styrenic copolymers, co-polyester polymers, co-polyamide polymers, a copolymer reaction product of polyaurinlactam and polytetrahydrofuran, and combinations thereof, and subsequently irradiated to provide a thermoset polymer before being formed into a finished product. Irradiating the composition causes the polymer to convert from a thermoplastic state to a thermoset state without encountering the risk of premature cross-linking that has plagued the above-discussed prior art compositions. The resulting thermoset polymer exhibits advantageous physical and chemical properties. For example, the thermoset polyurethane made in accordance with the present invention can be formulated advantageously to be essentially free of discoloration often associated with prior art thermoset polyurethanes made from TPUs. The term "essentially free of discoloration", as used herein, is intended to mean that the thermoset polyurethane of the present invention advantageously exhibits essentially none (or little) of the undesirable yellow, brown or orange discoloration that typically characterizes thermoset resins produced in accordance with the aforementioned prior art patents.

Illustrative of one class of polymers, the polyurethane is suitably irradiated to convert the thermoplastic polyurethane to a thermoset polyurethane is suitably effected using a beam of photons, preferably from a source of high energy ionizing photons, in order to cause cross-linking of the thermoplastic polyurethane composition to occur. The radiation source suitably provides the desired irradiation of the thermoplastic polyurethane. As used herein, the term "irradiation", in the context of the photon beam employed in the present invention,

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is used expansively to encompass bombardment of the target thermoplastic polyurethane with photons, e.g. beta (also referred to herein as e-beam) particles, gamma particles, ultraviolet ("uv") radiation, combinations thereof, and the like, in order to effect conversion of the TPU to the desired thermoset polyurethane.

- 5 Although the energy output from the radiation source to the thermoplastic polyurethane composition can vary over a wide range, it is preferred that, when using e-beam irradiation, an amount of radiation of from about 1 and about 100 Mega Rads, more preferably between 10 and 50 Mega Rads, most preferably between 10 and 20 Mega Rads, be imparted to the composition over a suitable
10 period of time to insure that the polyurethane being irradiated does not overheat.

As used herein, the term "thermoplastic" is used in its broad sense to designate a material that is reprocessable at an elevated temperature, whereas "thermoset" designates a material that exhibits high temperature stability without such reprocessability at elevated temperatures. The term "thermoplastic
15 elastomer" designates a material that possesses an elastic, rubber-like property such that it exhibits at least a one hundred percent elongation without breaking when stretched at room temperature, and will return to its unstretched length when released. Useful thermoplastics include extrudable solid polymers, powder coating polymers, as well as sprayable polymers.

- 20 As used herein, the term "allylic monomer" is intended to designate a cross-linking moiety for polyurethanes that is monomeric and contains an allyl group. Preferably, the allylic monomer is free of peroxide, acrylate, and methacrylate moieties.

Particularly useful reactive monomers include, for example,
25 triallylisocyanurate (also referred to herein as "TAIC"), triallylcyanurate (also referred to herein as "TAC"), diallyl phthalate (also referred to herein as "DAP"), and meta-phenylene dimaleimide (also referred to herein as MPDM), and combinations thereof. The TAIC is commercially available as a liquid dispersion, and, alternatively, on a silicate substrate (75% TAIC on 25% silicate) as SYNPRO
30 PLC-4185, a product of Synpron. Although less desired, other useful reactive

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monomers include methacrylate-containing monomers, such as trimethylolpropane trimethacrylate (TMPTMA), commercially available as Sartomer's SR-350.

When the selected polymer is a polyurethane, the reactive monomer is suitably admixed with the polyurethane-forming composition prior to preparation of the TPU, or admixed with the TPU prior to preparation of the desired thermoset polyurethane product.

Although not wishing to be bound by any particular theory, it is believed that the essentially discoloration-free appearance of the thermoset polyurethanes produced in accordance with the present invention is attributable to the use of an aliphatic polyisocyanate in the polyurethane-forming compositions employed in the present invention. The present inventor has found that the irradiation employed in the present invention does not significantly discolor the aliphatic polyisocyanate-based polyurethane compositions employed in this invention. In contrast, such irradiation appears to severely discolor comparison polyurethane compositions based upon aromatic polyisocyanates. Further, the present inventor has found that aliphatic polyisocyanate-based TPUs are suitably converted to thermoset compositions by irradiation, whereas the benzene molecules in backbone of aromatic polyisocyanate-based TPU's seem to absorb high energy radiation (e-beam or gamma rays), thus rendering aromatic isocyanate-based TPU's stable (and, hence, not easily thermoset) in the presence of irradiation. Moreover, although aromatic polyisocyanate-based TPU's typically exhibit better chemical properties, such as resistance to organic solvents and oils, than prior art aliphatic polyisocyanate-based TPU, the compositions of the present invention overcome this disadvantage since the thermoset polyurethanes of the present invention exhibit excellent physical and chemical properties.

The aliphatic polyisocyanate useful as a reactant in forming the polyurethanes employed in the present invention is preferably selected from commercially-available aliphatic polyisocyanates such as, for example, 1,6-hexamethylene diisocyanate ("HDI"), isophorone diisocyanate ("IPDI"), ethylene diisocyanate, 1,4-tetramethylene diisocyanate, 2,2,4-trimethyl-1,6-hexamethylene

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diisocyanate, 1,10-decanemethylene diisocyanate, 1,12-dodecanemethylene diisocyanate, cyclohexane-1,3-diisocyanate, cyclohexane-1,4-diisocyanate, 1-isocyanato-2-isocyanatomethyl cyclopentane, isophorone diisocyanate, *bis*-(4-isocyanatocyclohexyl)-methane, 1,3- and/or 1,4-*bis*-(isocyanatomethyl)-
5 cyclohexane, *bis*-(4-isocyanato-3-methyl-cyclohexyl)-methane, 1-isocyanato-1-methyl-4(3)-isocyanatomethyl cyclohexane, 4,4'-dicyclohexylmethane diisocyanate, and combinations thereof.

The "polyahl" useful as a reactant in forming the polyurethanes employed in the present invention is an active hydrogen-containing compound that is
10 reactive with the aliphatic polyisocyanate to produce the desired polyurethane. In addition, the term polyahl is intended to encompass compounds that react to generate an active hydrogen-containing moiety such as imines. An active hydrogen group is a group which has a hydrogen atom which, because of its position in the molecule, displays activity according to the Zerewitnoff test
15 described by Woller in the Journal of American Chemical Society, Vol. 49, page 3181 (1927). Illustrative of such active hydrogen groups are -OH, -NH-, -COOH, -SH and -CONH-. Particularly suitably polyahls include polyols, imines (such as ketimines and aldimines), oxazolidines, and combinations thereof, preferably having a weight average molecular weight of between about 100 and about
20 10,000, more preferably between about 100 and about 5,000, most preferably between about 200 and about 2,000.

Suitable amines are aliphatic or cycloaliphatic, primary or secondary amines. Preferred amines are poly(alkyleneoxy)alkylamines.

Suitable polyols include polyether polyols and polyester polyols. The
25 preferred polyols useful in the present invention have a hydroxyl functionality of no greater than about 2, more preferably less than 1.5, advantageously about 1, in order to prevent the formation of very high molecular weight polyurethane prepolymers which result in coating viscosities higher than desired for ready application. The polyether polyols are prepared by polymerization of alkylene
30 oxides with water, polyhydric alcohols with two to eight hydroxyl groups, or

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amines. Polyester polyols are suitably prepared by a condensation reaction of a polycarboxylic acid with a polyhydric alcohol. Another useful polyol is polybutadiene glycol ("PBDG").

In preparing the polyurethanes useful in the present invention, the ratio of
5 NCO equivalents in the polyisocyanate to the OH equivalents in the active hydrogen-containing compound can vary over a wide range of between about 10:1 and about 1:10, preferably between about 2:1 and about 1:2.

Catalysts are typically employed in the polyurethane-forming reaction. Useful catalysts include those which facilitate the reaction of the polyol with the
10 aliphatic polyisocyanate reactants. Suitable catalysts are the organotin catalysts, alone or in combination with amine catalysts, particularly tertiary amine catalysts. Illustrative organotin catalysts include dibutyltin dilaurate, stannous octoate, and combinations thereof. Illustrative amine catalysts include the following:
N,N'-dimethylethanolamine, N,N-dimethylamino-ethoxyethanol,
15 N,N'-dimethylaminoethyl-N-methylethanolamine,
N,N-dimethyl-N',N'-2-hydroxypropyl-1,3-propylene diamine,
N,N,N'-trimethyl-N'-hydroxyethyl-bis(amino ethyl) ether,
N,N-bis(3-dimethylaminopropyl) amino-2-propanol, and combinations thereof.
The catalysts are suitably employed in the polyurethane-forming formulation in a
20 total amount of between about 0.01% and about 5%, preferably between about 0.01% and about 1%, by weight based upon the weight of the polyurethane-forming composition.

In preparing the desired polyurethane, the polyether polyol(s), polyisocyanate(s), chain extender(s) such as polyether or polyester glycol chain
25 extenders, and other desired components are reacted, typically at an elevated temperature. One method of forming the desired thermoplastic polyurethane is by continuous processing utilizing an extruder, as illustrated by the disclosures of U.S. Patent 3,642,964, incorporated herein by reference in its entirety. An alternative method involves batch processing, followed by grinding and extrusion
30 of the formed elastomer as is well-known in the art. Although either the

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prepolymer method or the one-shot method can be used, the one-shot method is preferred. The one-shot method is intended to also include the process whereby the diisocyanate has been converted to a quasi-prepolymer by reaction with a minor amount (i.e., less than about 10 percent on an equivalent basis) of polyol
5 prior to carrying out the polyurethane forming reaction.

In preparing the desired polyurethane, urethane forming catalysts can be used, as discussed above, as well as the usual compounding ingredients such as antioxidants or other antidegradants. Typical antioxidants include hindered phenols, butylated hydroxytoluene ("BHT"), and the like. Other optional
10 compounding ingredients include, for example, plasticizers, adhesion promoters, fillers and pigments like clay, silica, fumed silica, carbon black, talc, phthalocyanine blue or green, TiO_2 , U-V absorbers, MgCO_3 , CaCO_3 and the like. The compounding ingredients are suitably employed in an amount of between 0 and about 75 weight percent based upon the weight of the elastomer. The
15 polymerization reaction may be carried out in a single reaction (one-shot process), or in one or more sequential steps (prepolymer process), using either bulk polymerization or solution polymerization. When solution polymerization is used, polar solvents such as tetrahydrofuran ("THF"), dimethylformamide ("DMF"), and dimethylacetamide ("DMAC") are typically utilized. In the
20 one-shot process, all the isocyanate-reactive components are reacted simultaneously with the polyisocyanate. In such process, it is normal practice to blend all components except the polyisocyanate into a "B-side" mixture, which is then reacted with the polyisocyanate to form the polyurethane and/or polyurea elastomer. However, the order of mixing is not critical as long as the components
25 do not undesirably react before all components are present. The reaction mixture is then suitably placed in a mold, or extruded through an extruder, and cured at a suitable temperature. The apparatus used for blending and molding is not especially critical. Hand mixing, conventional machine mixing, and the so-called reaction injection molding (RIM) equipment are all suitable. In the prepolymer
30 process, all or a portion of one or more of the isocyanate reactive materials is

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reacted with a stoichiometric excess of the polyisocyanate to form an isocyanate-terminated prepolymer. This prepolymer is then allowed to react with the remaining isocyanate-reactive materials to prepare the polyurethane and/or polyurea elastomer. The prepolymer can be prepared with either the polyether or
5 the chain extender, or a mixture of both.

The mixing of the reactants can be carried out at ambient temperature (typically from 20NC to 25NC) and the resulting mixture is then heated to a temperature of the order of about 40NC to about 130NC, preferably to a temperature of about 90NC to about 120NC. Alternatively, and preferably, one or
10 more of the reactants is preheated to a temperature within the above ranges before the admixing is carried out. Advantageously, in a batch procedure, the heated reaction components are subjected to degassing in order to remove entrained bubbles of air, water, or other gases before the reaction takes place. This degassing is accomplished conveniently by reducing the pressure under which the
15 components are maintained until no further evolution of bubbles occurs. The degassed reaction components are then admixed and transferred to suitable molds or extrusion equipment or the like and cured at a temperature of the order of about 20NC to about 115NC. The time required for curing will vary the temperature of curing and also with the nature of the particular composition, as is known in the
20 art.

The polymers produced in accordance with the present invention are useful in a variety of applications, including sealants, elastomers, coatings, adhesives, and in the fabrication of a wide variety of household, commercial, and industrial products. For example, the present invention is suitably employed to
25 produce crosslinked polymers that are useful in producing medical catheters, angioplasty balloons, and male and female birth control sheath products. The crosslinked polymer product retains its flexural modulus at body temperatures longer than catheters made from prior art TPU's. As another illustration, the present invention is suitably employed to produce flexible wire and cable jackets
30 having improved temperature and fluid resistance, as compared analogous

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products made from prior art TPU's. Other illustrative uses for the thermoset polymers produced in accordance with the present invention include the following: orthodontic ligatures which last longer than those made from prior art TPU's; seals, gaskets and o-rings which are easier to fabricate than those made from prior art cast polyurethanes and exhibiting better temperature stability, compression set and fluid resistance than those made from prior art TPU's; sneaker and shoe soles that are longer wearing than those made from prior art TPU's; longer lasting toner wiper blades for copiers and laser printers, as compared to those made from prior art TPU's; and, medical implanted devices and wires which last longer inside body parts and cavities than those made from prior art TPU's.

The polymer employed in the present invention is suitably shaped into the desired product configuration while in the thermoplastic state, and then irradiated to thermoset the polyurethane product. The thermoplastic polymer can be in solid form, such as pellets, prior to forming the desired polymer product. Alternatively, solid thermoplastic polymer can be dissolved in organic solvent, and used for dipping, spraying or otherwise coating the dissolved polymer onto a substrate, and then the coating is suitably thermoset by irradiation.

As used herein, the term "molecular weight" is intended to designate number average molecular weight. All percents used herein are percents by weight unless otherwise specified. As used herein, the term "phr" denotes "parts by weight per hundred parts of resin".

The following Example is intended to illustrate, but in no way limit the scope of, the present invention.

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EXAMPLE 1Part A - Preparation and Testing of a Thermoset Polyurethane of the Present Invention:

A sample of dried aliphatic polyester, thermoplastic polyurethane resin,
5 having a hardness of 80 Shore A and a melt index of 2 at 165EC, was
compounded with 4 phr of SYNPRO PLC-4185 (75% TAIC on 25% silicate)
allylic monomer to yield a mixture containing 3 phr TAIC. This mixture was
compression molded at 125EC for 10 minutes to yield a 6"x6"x.070" plaque. The
plaque was exposed to 14 Mega Rads of high energy electron beam irradiation in
10 order to convert the plaque to a thermoset plaque.

After irradiation the thermoset plaque was tested for various physical
properties in accordance with ASTM tests as identified in Table 1 below. The test
results are provided in Table 1.

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Table 1

Physical Properties	14 Mrads
Ultimate elongation at break (%)	425
200% Modulus (psi)	900
Compression set (%)	58.5 (72 hours at 100EC)
Color change (visual)	minimal

Fluid Resistance		14 Mrads	
Fluid	Temp	Time	Observation
Mil-L-16884	121EC	2.5 hrs	swell+13%, brown stained, somewhat tacky
Tetrahydrofuran	20EC	2.5 hrs	swelled, very friable, did not dissolve**
100% IPA*	20EC	2.5 hrs	no change
50% IPA*	20EC	2.5 hrs	no change
Water, distilled	20EC	2.5 hrs	no change

(* IPA=isopropyl alcohol)

5 (** unirradiated pellets completely dissolved)

Part B - Temperature Stability Test

The irradiated polyurethane of Part A above did not melt or flow at elevated temperatures as demonstrated by probing the irradiated plaque with an electrically heated solder iron tip at a temperature of approximately 300EC.

10

Part C - Comparison with Aromatic Polyisocyanate-based Polyurethanes.

Dow's PELLETHANE 55D aromatic polyisocyanate-based polyurethane resin was compounded with 3 phr TAIC allylic monomer, and exposed to 15 Mrads of high energy electron beam irradiation. No crosslinking was observed based upon the results of a hot iron test (described hereinabove) on this composition, and the physical properties were unchanged relative to the unirradiated neat pellets. Instead, the irradiated material discolored by turning dark brown.

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In a second experiment, Dow's PELLETHANE 55D aromatic polyisocyanate-based polyurethane resin Pellethane 55D was compounded with 3 phr of TMPTMA (an acrylic monomer) and exposed to 15 Mrads of high energy electron beam irradiation. No crosslinking was observed in the hot iron test as described above, and the physical properties were unchanged relative to the unirradiated neat pellets. The irradiated material turned dark brown.

Part D - Comparison of Crosslinked Versus Uncrosslinked TPUs in a Weighted Probe Test.

A comparison was made between the physical property stability of a crosslinked polymer and that of an uncrosslinked polymer when exposed to elevated temperatures using a Thermo-Mechanical Analyzer ("TMA"). Briefly, the test regimen was conducted by placing a small piece (approximately 2 millimeters thick) of polymer is heated to an elevated temperature in the TMA, and a round glass probe weighted to 5 grams is applied to the sample. The sample was heated in the TMA to provide a controlled rate of temperature increase of 5 degrees Centigrade per minute, and the resulting probe penetration into the sample of TPU was recorded as a function of time. The test results showed that the probe caused heat deformation of the uncrosslinked TPU at a much lower temperature than that at which it caused deformation of the crosslinked TPU. By way of illustration, uncrosslinked TPU was initially penetrated by the probe at a polymer temperature of 115 degrees Centigrade. In contrast, TPU exposed to 20 MRads of radiation before being placed in the TMA resisted initial penetration until a polymer temperature of 239 degrees Centigrade was reached. These results demonstrate the improved dimensional heat stability of the crosslinked TPU as compared to the uncrosslinked TPU.

EXAMPLE 2

Physical Property Testing of Block Copolymers Before and After Irradiation

Samples of several block copolymers were prepared and tested as follows: Each polymer identified in Table 1 below was mixed with 3% (by weight) of pure

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liquid TAIC (trialllyisocyanurate) in a twin screw extruder, and the resulting mixture was strand extruded and pelletized. The extruded product was dried and compression molded into plaques having dimensions of 6 inches x 6 inches x .080 inches, and then irradiated with electron beam irradiation at the indicated dosage shown in Table 1 below.

Tensile bars of the extruded product were die cut and the tensile strength and elongation at break for these samples were measured. The melting ability of these samples was determined by applying a hot instrument to them. The results are displayed in Table 1 below.

10

TABLE 2

Change in physical properties related to radiation
dose for certain modified polymers

Material	Dose	Color	Melts	Tb ^{**}	Eb ^{***}
Pebax-72D	0	white	yes	6460	190
"	10	green	no	6740	105
"	12.5	green	no	6770	95
"	15	green	no	6800	90
Hytril-72D	0	white	yes	4895	200
"	10	white	no	4890	170
"	12.5	white	no	4180	20
"	15	grey	no	4830	15

- 15 (Units are in MegaRads).
 (** Tensile strength at break in psi).
 (***) Elongation at break in percent).

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The results as provided in Table 2 above demonstrate that Hytril and PEBAX block co-polymers having a Shore D hardness of 72, exhibit changes in mechanical properties consistent with crosslinking of these polymers. The HYTRIL polymer is a co-polyester polymer of poly(1,4 butanediol terephthalate) and poly(alkylene ether terephthalate), whereas the PEBAX polymer is a co-poly(ether-ester-amide) polymer. Both polymers exhibit decreasing elongation with increasing radiation dose, and both no longer melt at the temperature tested, namely 325 degrees Centigrade, at high radiation doses. In addition, PEBAX polymer shows an increase in tensile strength with increased radiation dose, while the tensile strength of HYTRIL polymer is essentially unchanged with increased radiation dose.

While the invention has been described above with references to specific embodiments thereof, it is apparent that many changes, modifications and variations can be made without departing from the inventive concept disclosed herein. Accordingly, it is intended to embrace all such changes, modifications and variations that fall within the spirit and broad scope of the appended claims.

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1. A radiation-crosslinkable composition characterized by:
 - (a) a polymer selected from the group consisting of polyurethanes, styrene-based polymers, polyester-based polymers, polyether-based polymers, polyamide-based polymers, polylaurinlactam-based polymers, polytetrahydrofuran-based polymers, and combinations thereof, and
 - (b) a reactive monomer for cross-linking at least a portion of said polymer upon contacting said reactive monomer with energy from a radiation source.
2. The radiation-crosslinkable composition of claim 1 characterized in that said energy is in the form of free radical initiating or ionizing radiation particles selected from the group consisting of photons, beta-particles and gamma-particles, ultraviolet radiation, and combinations thereof.
3. The radiation-crosslinkable composition of claim 2 characterized in that said polymer of component (a) comprises a block co-polymer containing hard and soft segments, and wherein said ionizing radiation is in the form of ultraviolet or electron beam radiation.
4. The radiation-crosslinkable composition of claim 3 characterized in that said block co-polymer is selected from the group consisting of poly (1,4-butanediol terephthalate), styrenic co-polymers, co-polyester polymers, co-polyamide polymers, a reaction product of polylaurinlactam and polytetrahydrofuran, a reaction product of an aliphatic polyisocyanate and a polyol; and, combinations thereof.
5. The radiation-crosslinkable composition of claim 1 characterized in that said reactive monomer of component (b) is an allylic monomer cross-linker that is free of peroxide, acrylate and methacrylate moieties.
6. The radiation-crosslinkable composition of claim 1 characterized in that said reactive monomer of component (b) is selected from the group consisting of triallylisocyanurate, triallylcyanurate, diallyl phthalate, meta-phenylene dimaleimide, and combinations thereof.

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7. The radiation-crosslinkable composition of claim 4 characterized in that said aliphatic polyisocyanate is selected from the group consisting of 1,6-hexamethylene diisocyanate ("HDI"), isophorone diisocyanate ("IPDI"), ethylene diisocyanate, 1,4-tetramethylene diisocyanate, 2,2,4-trimethyl-1,6-hexamethylene diisocyanate, 1,10-decanemethylene diisocyanate, 1,12-dodecanemethylene diisocyanate, cyclohexane-1,3-diisocyanate, cyclohexane-1,4-diisocyanate, 1-isocyanato-2-isocyanatomethyl cyclopentane, isophorone diisocyanate, *bis*-(4-isocyanatocyclohexyl)-methane, 1,3- and/or 1,4-*bis*-(isocyanatomethyl)-cyclohexane, *bis*-(4-isocyanato-3-methyl-cyclohexyl)-methane, 1-isocyanato-1-methyl-4(3)-isocyanatomethyl cyclohexane, 4,4'-dicyclohexylmethane diisocyanate, and combinations thereof.

8. A process for preparing a thermoplastic article and for converting the thermoplastic article to a thermoset article, said process characterized by the steps of:

15 (a) preparing a thermoplastic polymer product by mixing a solid, extrudable thermoplastic polymer product with a solid or liquid reactive monomer cross-linker and a polymer selected from the group consisting of nylon, polyurethanes, styrene-based polymers, polyester-based polymers, polyether-based polymers, polyamide-based polymers, polylactam-based polymers, 20 polytetrahydrofuran-based polymers, and combinations thereof,

(b) forming said thermoplastic mixture into a desired thermoplastic article, and

(c) irradiating said article with a particle beam in order to cause said reactive monomer cross-linker in said product to cross-link at least a portion of 25 said polymer, thereby converting said article into a thermoset article, said thermoset article exhibiting enhanced properties relative to said thermoplastic article.

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9. The process of claim 8 characterized in that said solid thermoplastic polymer product adsorbs or absorbs said liquid reactive monomer, thus providing a solid thermoplastic mixture.
10. The process of claim 8 characterized in that said particle beam comprises
5 particles selected from the group consisting of photons, beta-particles and gamma-particles, and combinations thereof.
11. The process of claim 8 characterized in that said reactive monomer cross-linker of component (a) is selected from the group consisting of triallylisocyanurate, triallylcyanurate, diallyl phthalate, meta-phenylene
10 dimaleimide, and combinations thereof.
12. The process of claim 8 characterized in that said polymer of component (a) comprises a reaction product of an aliphatic polyisocyanate and a polyah.
13. The process of claim 8 characterized in that said polymer is a block co-polymer selected from the group consisting of poly(1,4-butanediol terephthalate),
15 styrenic co-polymers, co-polyester polymers, co-polyamide polymers, a reaction product of polyaurinlactam and polytetrahydrofuran, a reaction product of an aliphatic polyisocyanate and a polyahl; and, combinations thereof.
14. A process for producing a thermoset product which comprises irradiating a thermoplastic elastomer composition containing a reactive monomer cross-linker
20 in order to cross-link said thermoplastic elastomer to convert the thermoplastic elastomer to said thermoset product, said thermoplastic elastomer composition comprising a component selected from the group consisting of styrenic co-polymers, co-polyester polymers, co-polyamide polymers, a reaction product of polyaurinlactam and polytetrahydrofuran, a reaction product of an aliphatic
25 polyisocyanate and a polyahl; and, combinations thereof.

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15. A cross-linkable angioplasty balloon suitable for irradiation-induced cross-linking, said angioplasty balloon comprising a radiation-crosslinkable polymer composition characterized by (a) a component selected from the group consisting of nylon, styrenic co-polymers, co-polyester polymers, co-polyamide polymers, a
5 reaction product of polyaurinlactam and polytetrahydrofuran, a reaction product of an aliphatic polyisocyanate and a polyahl; and, combinations thereof, and (b) a reactive monomer cross-linker in an amount sufficient to provide cross-linking of at least a portion of said polymer or copolymer upon contacting said cross-linker with ionizing photons from a radiation source.

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16. A method of using an angioplasty balloon that is produced from a thermoplastic polymer converted to a thermoset polymer, characterized in that the balloon comprises the reaction product of a radiation-crosslinkable polymer composition comprising (a) a component selected from the group consisting of
- 5 nylon, poly(1,4-butanediol terephthalate), styrenic co-polymers, co-polyester polymers, co-polyamide polymers, a reaction product of polyaurinlactam and polytetrahydrofuran, a reaction product of an aliphatic polyisocyanate and a polyahl; and, combinations thereof, and (b) a reactive monomer cross-linker in an amount sufficient to provide cross-linking of at least a portion of said polymer or
- 10 copolymer upon contacting said cross-linker with radiation from a radiation source, said method comprising the steps of:
- (i) forming a tube from said radiation-crosslinkable polymer composition,
 - (ii) irradiating said tube with a beam of particles in order to cause said radiation-crosslinkable polymer composition to crosslink, thereby converting said
 - 15 tube from a thermoplastic to a thermoset state, said thermoset state exhibiting enhanced properties relative to said thermoplastic state,
 - (iii) heat expanding a portion of the tube to provide a balloon in said tube, and deflating said balloon,
 - (iv) inserting said tube containing said balloon, in a deflated state, into a
 - 20 desired blood vessel within a human or other mammal body, and moving said balloon to a desired site within said blood vessel, and
 - (v) inflating said balloon to an inflated state at said desired site to provide an inflated balloon.

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17. A process for fabricating a tube containing an angioplasty balloon from a crosslinkable polymer composition characterized by (a) a component selected from the group consisting of nylon, poly (1,4-butanediol terephthalate), styrenic co-polymers, co-polyester polymers, co-polyamide polymers, a reaction product of polyaurinlactam and polytetrahydrofuran, a reaction product of an aliphatic polyisocyanate and a polyahl; and, combinations thereof, and (b) a reactive monomer cross-linker in an amount sufficient to provide cross-linking of at least a portion of said polymer or copolymer upon contacting said cross-linker with radiation from a radiation source, said process comprising the steps of:
- 5
- 10 (i) forming a tube from said radiation-crosslinkable polymer composition,
- (ii) irradiating said tube with a beam of particles in order to cause said radiation-crosslinkable polymer composition to crosslink, thereby converting said tube from a thermoplastic to a thermoset state, said thermoset state exhibiting enhanced properties relative to said thermoplastic state,
- 15 (iii) heat expanding a portion of the tube to provide a balloon in said tube, and deflating said balloon, thus forming said tube containing said angioplasty balloon.
18. The method of claim 16 characterized in that said balloon comprises crosslinked nylon in said thermoset state.
- 20 19. The method of claim 16 characterized in that said reactive monomer cross-linker is an allylic monomer cross-linker that is free of peroxide, acrylate and methacrylate moieties.
20. The method of claim 16 characterized in that said polyahl is a polyol being polybutadiene glycol.
- 25 21. The method of claim 16 characterized in that said beam of particles is selected from the group consisting of beta particles, gamma particles, ultraviolet radiation, and combinations thereof.

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22. The method of claim 16 characterized in that said beam of particles imparts between about 1 and about 100 Mega Rads of energy to said composition.

23. The method of claim 16 characterized in that said reactive monomer is selected from the group consisting of triallylisocyanurate, triallylcyanurate, diallyl
5 phthalate, meta-phenylene dimaleimide, and combinations thereof.

24. The product produced by the process of claim 14, said product being formed into a device selected from the group consisting of medical catheters, surgical gloves, angioplasty balloons, birth control sheathes, heat shrinkable tubing, heat-shrinkable film, and combinations thereof.

10 25. A method of forming a coated substrate characterized by a substrate and a coating on said substrate, said method comprising applying said coating to said substrate in a thermoplastic state, and converting said coating to a thermoplastic state by free radical initiated crosslinking of the coating in the presence of heat or particle beam radiation selected from the group consisting of electron beam
15 radiation, uv radiation, or a combination thereof, to provide a thermoset coating on said substrate characterized by enhanced bonding efficacy to said substrate in said thermoset state relative to said thermoplastic state.

26. The method of claim 25 characterized in that said substrate is selected from the group consisting of metal, glass, plastic, wood, paper, and combinations
20 thereof.

27. The method of claim 25 characterized in that said coating comprises a polymer selected from the group consisting of polyurethanes, styrene-based polymers, polyester-based polymers, polyether-based polymers, polyamide-based polymers, polylaurinlactam-based polymers, polytetrahydrofuran-based polymers,
25 and combinations thereof.

28. The coated substrate produced by the method of claim 25.

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29. In a method of forming a composite characterized by two substrates with a coating therebetween, the improvement characterized by contacting one side of each of said two substrates with said coating in a thermoplastic state, and converting said coating to a thermoset state crosslinking of the coating in the presence of radiation selected from the group consisting of electron beam radiation, uv radiation, or a combination thereof, to provide said composite, wherein the thermoset coating in said composite is characterized by enhanced bonding efficacy to said two substrates relative to said thermoplastic state.
30. The method of claim 29 characterized in that said substrates are independently selected from the group consisting of metal, glass, plastic, wood, paper, and combinations thereof.
31. The method of claim 29 characterized in that said coating comprises a polymer selected from the group consisting of polyurethanes, styrene-based polymers, polyester-based polymers, polyether-based polymers, polyamide-based polymers, polylaurinlactam-based polymers, polytetrahydrofuran-based polymers, and combinations thereof.
32. The composite produced by the method of claim 29.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/18163

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : Please See Extra Sheet.

US CL : Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : Please See Extra Sheet.

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X -- Y	US 3,719,539 A (LAMB et al.) 06 March 1973, abstract and columns 1 and 2.	1-14,25-32 ----- 15-24
A	US 3,911,202 A (STINE et al) 07 October 1975.	1-32
X -- Y	US 4,013,806 A (VOLKERT et al) 22 March 1977, columns 3-7.	1-14,25-28 ----- 15-24,29-32
X -- Y	US 4,065,589 A (LENARD et al) 27 December 1977, abstract and columns 2 and 3.	1-14,25-28 ----- 15-24,29-32

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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O document referring to an oral disclosure, use, exhibition or other means	
P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

12 DECEMBER 1997

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12 JAN 1998

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INTERNATIONAL SEARCH REPORT

 International application No.
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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X -- Y	US 4,101,699 A (STINE et al) 18 July 1978, abstract and columns 2-5.	1-14,25-28 ----- 15-24,29-32
X -- Y	US 4,264,658 A (TOBIAS et al) 28 April 1981, abstract and columns 2-4.	1-14,25-28 ----- 15-24,29-32
X -- Y	US 4,266,005 A (NAKAMURA et al) 05 May 1981, abstract and columns 2-11.	1-14,25-32 ----- 15-24
A	US 4,275,180 A (CLARKE) 23 June 1981.	1-32
X -- Y	US 4,654,233 A (GRANT et al) 31 March 1987, abstract and columns 3-13.	1-14,25-28 ----- 15-24,29-32
X -- Y	US 4,687,689 A (YAZAKI et al) 18 August 1987, abstract and columns 3-11.	1-14,25-28 ----- 15-24,29-32
X -- Y	US 4,762,884 A (GOYERT et al) 09 August 1988, abstract and columns 3-11.	1-14 ----- 15-32
X -- Y	US 4,820,782 A (UENO) 11 April 1989, abstract and columns 2 and 3.	1-14 ----- 15-32
X -- Y	US 4,871,811 A (GAKU et al) 03 October 1989, abstract and columns 2-4.	1-14,25-32 ----- 15-24
X -- Y	US 5,284,883 A (UENO et al) 08 February 1994, abstract and columns 1-3.	1-14 ----- 15-32
X -- Y	US 5,455,308 A (BASTIAANSEN) 03 October 1995, abstract and columns 2-6.	1-14 ----- 15-32
Y, P	US 5,576,072 A (HOSTETTLER et al) 19 November 1996, column 3, lines 44-62.	15-24

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US97/18163

A. CLASSIFICATION OF SUBJECT MATTER:

IPC (6):

A41D 19/00; A61F 6/04; A61M 29/04; B32B 15/08, 17/10, 21/08, 25/08, 25/14, 27/08, 27/10, 27/28, 27/30, 27/34, 27/36, 27/40, 31/28; C08F 8/00, 8/30, 12/08, 257/02, 267/06, 267/10, 269/00, 271/00, 283/00, 283/01, 283/04, 283/06, 287/00, 291/06, 291/12; C08G 18/82, 63/88, 63/91, 65/46, 65/48, 69/46, 69/48; C08J 3/24, 3/28, 7/18

A. CLASSIFICATION OF SUBJECT MATTER:

US CL :

2/159, 161.7, 167, 168; 128/844; 156/272.2, 275.5, 275.7; 427/487, 488, 491, 496, 501, 505, 506, 507, 508, 513, 516, 520; 428/411.1, 423.1, 425.1, 425.6, 425.8, 431, 435, 441, 458, 461, 474.4, 477.7, 479.3, 479.6, 480, 481, 482, 500, 511, 523; 522/90, 96, 113, 114, 116, 135, 136, 138, 139, 140, 160, 164, 165, 166, 168, 173, 176, 178, 179, 181, 188; 525/50, 123, 127, 128, 165, 175, 176, 178, 181, 182, 183, 193, 241, 279, 281, 282, 304, 306, 311, 313, 333.3, 333.6, 374, 375, 383, 386, 417, 426, 445, 455, 529, 530, 539, 540; 528/75, 288, 289, 326, 327, 345, 363, 392, 405, 417, 421, 423, 425

B. FIELDS SEARCHED

Minimum documentation searched

Classification System: U.S.

2/159, 161.7, 167, 168; 128/844; 156/272.2, 275.5, 275.7; 427/487, 488, 491, 496, 501, 505, 506, 507, 508, 513, 516, 520; 428/411.1, 423.1, 425.1, 425.6, 425.8, 431, 435, 441, 458, 461, 474.4, 477.7, 479.3, 479.6, 480, 481, 482, 500, 511, 523; 522/90, 96, 113, 114, 116, 135, 136, 138, 139, 140, 160, 164, 165, 166, 168, 173, 176, 178, 179, 181, 188; 525/50, 123, 127, 128, 165, 175, 176, 178, 181, 182, 183, 193, 241, 279, 281, 282, 304, 306, 311, 313, 333.3, 333.6, 374, 375, 383, 386, 417, 426, 445, 455, 529, 530, 539, 540; 528/75, 288, 289, 326, 327, 345, 363, 392, 405, 417, 421, 423, 425

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Minimum documentation searched

Classification System: U.S.

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